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UNPUBLISHED PRELIMINARY DATA

ELECTRONIC STATES OF MOLECULES *

I. SELF-CONSISTENT FIELD CALCULATIONS OF THE
GROUND, IONIZED AND EXCITED STATES OF N_2 AND O_2

by

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Summary: A number of electronic states of N_2 and O_2 have been computed using the self-consistent field molecular orbital (SCF MO) method. The calculated ionization, excitation and total energies are compared with the available experimental data as well as with those reported by other workers.

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I. INTRODUCTION:

Since the introduction of Roothaan's self-consistent field procedure⁽¹⁾ for the calculation of the wave functions and energies of closed-shell electronic states of molecules, a number of such calculations⁽²⁻⁷⁾ have appeared in the literature. Pople and Nesbet⁽⁸⁾ have extended the above procedure to open-shell states and Nesbet⁽⁹⁾ has applied it to the π -electron system of butadiene. An ab initio calculation by Sahni⁽¹⁰⁾ for states of N_2^+ appears to be one of the earliest involving all electrons of open-shell states. Most calculations of the energies of excited states, however, have employed Mulliken's method⁽¹¹⁾ of approximating excited states and their energies from the ground state orbitals.

There has been some further development of SCF MO theory for open-shell states. Roothaan has recently given a procedure⁽¹²⁾ applicable to certain types of open-shell states. One limitation of this procedure, pointed out by Roothaan, is that it destroys the orbital picture and enables one to calculate only the

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1. Roothaan, C. C. J., Revs. Mod. Phys. 23, 69 (1951).
 2. Mulligan, J. F., J. Chem. Phys. 19, 347 (1951).
 3. Sahni, R. C., Trans. Faraday Soc. 49, 1246 (1953).
 4. Scherr, C. W., J. Chem. Phys. 23, 569 (1955).
 5. Sahni, R. C., J. Chem. Phys. 25, 33 (1956).
 6. Ransil, B. J., Revs. Mod. Phys. 32, 245 (1960).
 7. Yoshizumi, Hiroyuki, "Advances in Chemical Physics, Vol. II," page 359, Interscience Publishers, Inc., New York (1959).
References from 1938-1958 on SCF MO calculations are given.
 8. Pople, J. A. and Nesbet, R. K., J. Chem. Phys. 22, 571 (1954).
 9. Nesbet, R. K., Proc. Roy. Soc. (London) A230, 322 (1955).
 10. Sahni, R. C., Scientific Rept. No. 21, Feb. 1, 1955, Contract AF 19(122)-470, Dept. of Physics, University of Western Ontario.
 11. Mulliken, R. S., J. Chim. Phys. 46, 497 (1949).
 12. Roothaan, C. C. J., Revs. Mod. Phys. 32, 179 (1960).

total energy of the open-shell state. To the writers' knowledge, the only reported calculation employing Roothaan's open-shell procedure is one for the ground state of the OH molecule⁽¹³⁾, where the variational equations assume a particularly simple form. The concept of physically-meaningful orbitals is preserved in the LCAO SCF open-shell procedure outlined by Nesbet⁽¹⁴⁾. Therefore, it has been considered worthwhile to test the usefulness of this procedure by applying it to the calculation of a number of electronic states of diatomic molecules from first principles. In this series of papers, calculations of the ground and a number of ionized and excited states of diatomic molecules will be reported. The present paper deals with the electronic states of homopolar molecules N_2 and O_2 . Subsequent papers will deal with the electronic states of polar molecules, hydrides and molecular negative ions.

II. EQUATIONS FOR SELF-CONSISTENT FIELD MOLECULAR ORBITALS

Self-consistent field equations for the molecular orbitals (MO's) constituting an electronic state of a molecule are found by minimizing the energy over the total state function taken as the antisymmetrized product of independent molecular spin orbitals (MSO's). Each molecular orbital ϕ_i , can be expressed as a linear combination of atomic orbitals, χ 's, thus

$$\phi_i = \sum_p a_{ip} \chi_p \quad (1a)$$

where the a_{ip} are undetermined coefficients. Equation (1a) in matrix notation is expressed as

13. Freeman, A. J., *Revs. Mod. Phys.* 32, 273 (1960).

14. Nesbet, R. K., *Proc. Roy. Soc. (London)* A230, 312 (1955).

$$\phi_1 = a_1 \chi \quad (1b)$$

The equations for the undetermined coefficients are then given^(1,8) as

$$(\underline{H} + \underline{J} - \underline{K}^\alpha) \underline{a}_1^\alpha = \epsilon_1^\alpha \underline{S} \underline{a}_1^\alpha \quad (2)$$

$$(\underline{H} + \underline{J} - \underline{K}^\beta) \underline{a}_1^\beta = \epsilon_1^\beta \underline{S} \underline{a}_1^\beta \quad (3)$$

where the elements of matrices \underline{S} , \underline{H} , \underline{J} and \underline{K}^α or \underline{K}^β are defined as follows:

$$S_{pq} = \int \bar{\chi}_p \chi_q d\tau \quad (4)$$

$$H_{pq} = \int \bar{\chi}_p H \chi_q d\tau \quad (5)$$

$$J_{pq} = \sum_{r,t} \left(\sum_i^{\alpha} \bar{a}_{ri} a_{ti} + \sum_i^{\beta} \bar{a}_{ri} a_{ti} \right) \iint \bar{\chi}_p(1) \bar{\chi}_r(2) \frac{1}{r_{12}} \chi_q(1) \chi_t(2) d\tau_1 d\tau_2 \quad (6)$$

$$K_{pq}^{\alpha(\beta)} = \sum_{r,t} \left(\sum_i^{\alpha(\beta)} \bar{a}_{ri} a_{ti} \right) \iint \bar{\chi}_p(1) \bar{\chi}_r(2) \frac{1}{r_{12}} \chi_t(1) \chi_q(2) d\tau_1 d\tau_2 \quad (7)$$

In equation (5), H_{pq} is the element of the one-electron bare nuclear Hamiltonian matrix.

The secular equations corresponding to the self-consistent conditions (2) and (3) can be written

$$|\underline{F}^\alpha - \epsilon^\alpha \underline{S}| = 0 \quad \text{and} \quad |\underline{F}^\beta - \epsilon^\beta \underline{S}| = 0 \quad (8)$$

where

$$\underline{F}^{\alpha(\beta)} = \underline{H} + \underline{J} - \underline{K}^{\alpha(\beta)} \quad (9)$$

Equations (8) are solved iteratively until self-consistency is achieved for both the α and β spin sets.

For the closed-shell or paired-electron states, the solutions of equation (2) and (3) become identical and only one of these need be solved iteratively. If

the number of electrons, n_α , with α spin is not equal to the number, n_β , with β spin, or in the general open-shell state with unpaired electrons, one needs to solve both equations (2) and (3) for the undetermined coefficients \underline{a}_1^α and \underline{a}_1^β . Though these equations represent separate pseudo-eigenvalue problems, they are related through the dependence of \underline{J} upon both \underline{a}_1^α and \underline{a}_1^β , and are best solved simultaneously in an iterative fashion⁽⁸⁾.

The procedure whereby equations (2) and (3) are solved, respectively, for n_α and n_β eigenvalues and vectors is called the generalized or unrestricted treatment and results, for open-shell states, in $\epsilon_1^\alpha \neq \epsilon_1^\beta$ and $\underline{a}_1^\alpha \neq \underline{a}_1^\beta$ for paired orbitals. The resulting generalized wave function is an eigenfunction of the total Hamiltonian \mathcal{H} and of the spin component operator S_z , but is not an eigenfunction of the total spin operator, S^2 . This is due to the fact that the \underline{a}_1^α and \underline{a}_1^β and hence the space functions obtained as solutions of equations (2) and (3) are not identical for the paired spin orbitals (MSO). To obtain a pure spin state, the \underline{a}_1^α and \underline{a}_1^β for paired occupied MSO's can be restricted to be identical at each step of the SCF calculations. This procedure, called the restricted treatment, results in doubly-occupied MO's where the paired electrons have the same space function but different energies. It will be shown that the above restriction does not affect the results to any appreciable extent and is justified to obtain the proper spin character of the state.

III. COMPUTATIONAL DETAILS

A. Units

All the integrals and orbital energies have been calculated in atomic units (a.u.). For comparison with experimental data, the ionization and excitation energies are expressed in electron volts (e.v.). The following conversion factors have been employed.

$$\begin{aligned}
 1 \text{ a.u. (distance)} &= 0.52917 \text{ \AA} \\
 1 \text{ a.u. (energy)} &= 27.204 \text{ e.v.} \\
 1 \text{ e.v.} &= 8068.3_2 \text{ cm}^{-1}
 \end{aligned}$$

B. Atomic Orbitals

The AO's used are the real normalized Slater AO's, namely

$$\begin{aligned}
 1s &= (\zeta_1^3/\pi)^{1/2} \exp(-\zeta_1 r) \\
 2s &= (\zeta_2^5/3\pi)^{1/2} r \exp(-\zeta_2 r) \\
 \left. \begin{matrix} 2p_z \\ 2p_x \\ 2p_y \end{matrix} \right\} &= (\zeta_2^5/\pi)^{1/2} r \exp(-\zeta_2 r) \begin{cases} \cos \theta \\ \sin \theta \cos \phi \\ \sin \theta \sin \phi \end{cases} \quad (10)
 \end{aligned}$$

with the exception that an orthogonal $2s$ function was constructed on each atom using the expression

$$2s_o = (1-S^2)^{-1/2} \cdot [(2s) - S(1s)] \quad (11)$$

where $2s_o$ represents the orthogonal $2s$ function and $S = (1s | 2s)$.

Unless otherwise specified, all references to a $2s$ function are to the orthogonal functions. For convenience, the "o" subscript has been dropped. With this modification, the AO's on each atom now form an orthonormal set.

For the orbital exponents ζ_1 and ζ_2 , Slater's values are used, namely

	<u>N</u>	<u>O</u>
ζ_1	6.7	7.7
ζ_2	1.95	2.275

The Z-axes, centered on each atom, lie along the internuclear axis, with positive Z-directions toward each other.

C. Symmetry Orbitals

The LCAO MO's of a homopolar molecule belong in sets to irreducible representations of the point group $D_{\infty h}$. To obtain proper symmetry for these MO's,

symmetry orbitals are introduced. They are linear combinations of atomic orbitals of the correct symmetry and are given in Table 1.

TABLE 1

$\sigma_g 1s = 2^{-1/2} (1s + 1s')$	$\sigma_u 1s = 2^{-1/2} (1s - 1s')$
$\sigma_g 2s = 2^{-1/2} (2s + 2s')$	$\sigma_u 2s = 2^{-1/2} (2s - 2s')$
$\sigma_g 2p = 2^{-1/2} (2p_z + 2p_z')$	$\sigma_u 2p = 2^{-1/2} (2p_z - 2p_z')$
$\pi_u 2p = 2^{-1/2} (2p_x + 2p_x')$	$\pi_g 2p = 2^{-1/2} (2p_x - 2p_x')$
$\bar{\pi}_u 2p = 2^{-1/2} (2p_y + 2p_y')$	$\bar{\pi}_g 2p = 2^{-1/2} (2p_y - 2p_y')$

The LCAO MO's of a given symmetry are then constructed from basic symmetry orbitals of the same symmetry e.g.

$$1\sigma_g = a_{11} \sigma_g 1s + a_{12} \sigma_g 2s + a_{13} \sigma_g 2p$$

The ten MO's which can be formed from the chosen basis fall into the six symmetry classes or species labelled as σ_g , σ_u , π_u , π_g , $\bar{\pi}_u$ and $\bar{\pi}_g$. Three MO's each belong to σ_g and σ_u and one each to the others.

D. Interaction Integrals

All the integrals required in the evaluation of the matrix elements of the secular equation were evaluated by a program written for the CDC 1604 computer provided to us by Dr. J. C. Browne of the Dept. of Chemistry, University of Texas. These integrals were checked with the values calculated from the tables of integrals computed by Sahni and Cooley⁽¹⁵⁾. All the integrals are evaluated

15. Sahni, R. C. and Cooley, J. W., NASA Technical Note D-146, December 1959 - Supplements I, II, III(a) and III(b).

with an accuracy of six decimal places.

E. Electron Configurations

The electronic configuration of the different states considered in this study are given in Table 2, where the symbols + and - denote electrons with α spin and β spin respectively. In these calculations a single AP (anti-symmetrical product) function or electronic configuration is used for each state.

TABLE 2

ELECTRON CONFIGURATIONS

STATE	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_u$	$1\pi_u^-$	$1\pi_g$	$1\pi_g^-$	$3\sigma_u$
$N_2 (X^1 \Sigma_g^+)$	+	-	+	-	+	-	+	-		
$N_2 (A^3 \Sigma_u^+)$	+	-	+	-	+	-	+			+
$N_2 (B^3 \pi_g)$	+	-	+	-	+	+	-	+	-	+
$N_2 (C^3 \pi_u)$	+	-	+	-	+	+	-	+	-	+
$N_2^+ (X^2 \Sigma_g^+)$	+	-	+	-	+	+	-	+	-	
$N_2^+ (B^2 \Sigma_u^+)$	+	-	+	-	+	+	-	+	-	
$O_2 (X^3 \Sigma_g^-)$	+	-	+	-	+	-	+	-	+	+
$O_2 (a^1 \Delta_g)$	+	-	+	-	+	-	+	-	+	-
$O_2^+ (X^2 \pi_g)$	+	-	+	-	+	+	-	+	-	+
$O_2^+ (a^4 \pi_u)$	+	-	+	-	+	+	-	+	-	+

F. Automatic Computation

Generalized Treatment

In the generalized Hartree-Fock treatment described earlier, molecular

states represented by a single antisymmetrical product wave function should satisfy the equations

$$(\underline{F}^\alpha - \epsilon^\alpha \underline{S}) \underline{a}_1^\alpha = 0 \quad ; \quad (\underline{F}^\beta - \epsilon^\beta \underline{S}) \underline{a}_1^\beta = 0 \quad (12)$$

The elements of \underline{F} in equation (12) depend, at each stage of the iterative solution, upon the assumed \underline{a}_1 and the one and two center integrals over the atomic orbitals. Furthermore, since the generation of \underline{F} involves a summation over occupied molecular orbitals, a definite electronic configuration must be assumed for the given state.

It is convenient to introduce in equations (6) and (7) the simplified notation

$$c_{rt}^\alpha = \sum_1^\alpha \bar{a}_{r1} a_{t1} \quad ; \quad c_{rt}^\beta = \sum_1^\beta \bar{a}_{r1} a_{t1} \quad (13)$$

where the summation is over occupied orbitals ϕ_1 . Then we re-express the elements of \underline{G}^α and \underline{G}^β as follows

$$G_{pq}^{\alpha(\beta)} = \sum_{r,t} (c_{rt}^\alpha + c_{rt}^\beta) J_{pqrt} - \sum_{r,t} c_{rt}^{\alpha(\beta)} K_{pqrt} \quad (14)$$

The J_{pqrt} and K_{pqrt} are fixed by the internuclear distance and the choice of a χ basis. In the case of diatomic molecules, where the 1s, 2s, 2pz, 2px and 2py Slater functions on each atom are used, there are in general 27 unique non-vanishing rt combinations for each of the 27 unique pq elements, those with $r \neq t$ appearing twice in equation (14) due to symmetry considerations. These fixed interactions are conveniently stored in a 27 x 27 tabular form for systematic multiplication by the c_{rt} variables at each iteration.

Self-consistency is achieved in the overall solution when the \underline{a}_1 from successive iterations agree within predetermined limits. Alternatively, precision of the eigenvalues may be adopted as a more convenient criterion of the consistency.

Agreement of the eigenvalues of the successive cycles up to six decimal places was adopted as a criterion of self-consistency in these computations.

Restricted Treatment

The restricted treatment for open-shells is an abbreviated method which presumes that paired electrons have the same space functions, that is, $a_1^\alpha = a_1^\beta$, and, therefore, the solution for the smaller spin set is contained within that of the larger. The procedure is to solve iteratively the secular equation for the larger spin set, denoted by α . When self-consistency is attained, we have the ϵ_1^α and a_1^α and for the paired orbitals, $a_1^\beta = a_1^\alpha$. A final solution of the β secular equation using the self-consistent a_1^α gives the required ϵ_1^β . The resulting orbital energies and coefficients are almost identical with those obtained from the generalized treatment.

In both procedures we impose the further constraint of identical space functions for degenerate π and $\bar{\pi}$ molecular orbitals.

IV. SCF RESULTS

A number of different electronic states of O_2 and N_2 were studied using the procedures described in the preceding section. Both the generalized and restricted treatments were applied to each open-shell state to show that the constraint of identical space functions for electrons with paired spin does not appreciably affect the results. For closed shells the treatment follows that developed by Roothaan. The various ionized and excited states of the same molecule were computed at the equilibrium internuclear distance of the ground state.

The SCF LCAO MO energies and eigenvector coefficients for the various states of N_2 and O_2 using the restricted treatment are presented in Tables 7 - 16 given in Appendix I. The SCF MO's for these molecules are given in terms of the basic symmetry orbitals described earlier.

V. DISCUSSION

A. Total Energy

The total energies of the various electronic states of H_2 and O_2 were computed using the equations given in Appendix II and are presented in Table 3 along with the observed total energies. The percentage accuracy of each result is also reported in the table. The agreement in every case seems to be reasonably good considering the limited set of basic atomic functions used in these calculations. The calculated total energy for O_2 ($X^3\Sigma_g^-$), an open-shell state, is lower by 2.30 ev. than that previously reported for a single configuration⁽¹⁶⁾. The percentage accuracy of the calculations for the different states varies in a narrow range of 99.00 to 99.23 %. It is thus clear from the results listed in Table 3 that the above procedure for the calculation of the total energy of the open-shell states gives results of the same order of accuracy as Roothman's procedure for closed-shell states.

B. Excitation and Ionization Energies

Excitation as well as ionization energies represent the difference in total energy between two states of the same molecule. Computed total energies, however, include correlation errors which arise from the neglect, in the LCAO SCF calculations, of the spatial arrangement of the electrons. These correlation errors, moreover, appear to be a function of internuclear distance. Therefore, for the comparison of calculated and observed ionization and excitation energies, calculations of the different states of the same molecule were performed at the same internuclear distance. Correlation errors in the resulting vertical transition energies thus tend to cancel and these vertical results can be more favorably compared with experiment.

16. Kotani, M., Mizuno, Y., Kayama, K. and Ishiguro, E., J. Phys. Soc. (Japan) 12, 707 (1957).

TABLE 3

TOTAL ENERGIES OF ELECTRONIC STATES * OF N_2 AND O_2

Molecular State	This Calculation	Observed ^c	cal/obs ^o /o
$N_2, X \ 1\sum_g^+$	-108.573,572 ^a	-109.618	99.05
$A \ 3\sum_u^+$	-108.309,100	-109.335	99.06
$B \ 3\pi_g$	-108.298,274	-109.319	99.07
$C \ 3\pi_u$	-108.108,545	-109.204	99.00
$N_2^+, X \ 2\sum_g^+$	-108.029,387	-109.045	99.07
$B \ 2\sum_u^+$	-107.843,229	-108.932	99.00
$O_2, X \ 3\sum_g^-$	-149.092,076 ^b	-150.40966	99.12
$a \ 1\Delta_g$	-149.010,520	-150.373	99.09
$O_2^+, X \ 2\pi_g$	-148.694,117	-149.961	99.16
$a \ 4\pi_u$	-148.668,197	-149.818	99.23

* All electronic states of N_2 and O_2 are calculated at the internuclear distances $R = 2.0675$ a.u. and $R = 2.28167$ a.u., respectively.

^a This result compares with the analogous results -108.574 a.u. and -108.57362 a.u. reported by Scherr (4) and Ransil (6), respectively.

^b Kotani (16) reported a value of -149.00734 a.u. for a single configuration.

^c Computed using the observed ground state energy and observed vertical transition energies (17, 19, 20).

17. Herzberg, G. T., "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., Princeton, New Jersey, (1950).

Thus, in Tables 4 and 5, the vertical excitation and ionization energies, respectively, were computed using the total energy difference as well as by means of Koopmans' treatment⁽¹⁸⁾. These calculated values are compared with the observed vertical transition energies. When one considers that each calculated transition energy represents the difference of two equally large numbers, the results are seen to be in fair agreement with experiment.

The observed vertical excitation energies were taken from the Rydberg-Klein Rees (RKR) potential energy data for N_2 and O_2 published by Vanderslice and co-workers (19,20). The RKR method⁽²¹⁾ is an elegant means of obtaining the classical turning points for each vibrational level, v_1 , of a molecular state from the spectroscopic constants ω_1 , ωx_1 , α_1 , B_1 and D_1 for that level. The resulting potential energy curves for states of N_2 and O_2 are given in Figs. 1 and 2, respectively. The observed vertical excitation energies were obtained by taking the energy difference between potential curves along the vertical line through $R=R_e$ (ground).

The experimental values of vertical ionization energies comparable to our computed results are probably somewhat less than photon-impact values and closer to those obtained from spectra. The latter values, where available, are taken from the convergence limits of Rydberg series in the far UV spectra of molecules. Where both types of results are available, the difference is so small that either value may be used for comparison with the calculated value.

18. Koopmans, T., *Physics*, 1, 104 (1933).

19. Vanderslice, J. T., Mason, E. A., Lippincott, E. R., *J. Chem. Phys.* 30, 129 (1959).

20. Vanderslice, J. T., Mason, E. A., Maisch, W. G., *J. Chem. Phys.* 32, 515 (1960).

21. Vanderslice, J. T., Mason, E. A., Maisch, W. G., Lippincott, E. R., *J. Mol. Spectroscopy* 3, 17 (1959); *ibid.* 5, 83 (1960).

The Koopmans theorem has been applied with considerable success to the process of ionization⁽⁹⁾, and is basic to most calculations of excitation energies reported to date. In its most general form, Koopmans' theorem states that the energy expended in a single electron transition is very closely the difference in the initial and final energies of the electron being considered. This treatment assumes that changes in the wave functions of the other electrons are negligible or cancel each other. For the process of ionization, the final energy of the electron, by convention, is taken to be zero. Thus the ionization energy for a molecule becomes merely the negative of the initial orbital energy of the electron. By extension, the excitation energy is the difference in orbital energies of the given electron in its initial and final states. For ionization energies, the agreement with experiment is known to be quite good. The present results demonstrate that Koopmans' theorem is equally useful in discussing excitation energies.

TABLE 4
VERTICAL EXCITATION ENERGIES (ev)

MOLECULAR STATE	$E^* - E^0$ ^a	$\epsilon_a^* - \epsilon_1^0$ ^b	OTHER CALCULATION ^c	OBSERVED ^d
N ₂ , A $3\Sigma_u^+$	7.19	7.25	6.5	7.70
B $3\pi_g$	7.49	7.45	8.1	8.12
C $3\pi_u$	12.65	12.66	13.2	11.25
O ₂ , a $1\Delta_g$	2.22	2.16	—	1.0

^a Total energy of excited state minus total energy of ground state.

^b Difference in energy of excited state orbital ϕ_a^* and ground state orbital ϕ_1^0 .

^c Calculated using unoccupied ground state orbitals as in reference 4 for N₂.

^d From RKR potential energy data, references 19 and 20.

TABLE 5
VERTICAL IONIZATION ENERGIES (ev)

MOLECULAR STATE	$E^+ - E^0$ ^a	$-a_1^0$	OBSERVED ^b
$N_2^+, X \ ^2\Sigma_g^+$	14.80	14.81	15.576
$N_2^+, B \ ^2\Sigma_u^+$	19.88	19.87	18.72
$O_2^+, X \ ^2\Pi_g$	10.82	10.80	12.2
$O_2^+, a \ ^4\Pi_u$	11.53	11.50	16.1

^a Total energy of ionized state minus total energy of ground state.

^b Values, unless otherwise stated, are from Herzberg, reference 17, Tables 37 and 39.

C. Generalized and Restricted Treatments

It was stated previously that the generalized wave function for an open-shell molecular state necessitates solution of a pair of secular equations, the so-called generalized treatment. Since the resulting space functions of paired α and β electrons are generally different, these generalized solutions are not eigenfunctions of S^2 , though they are eigenfunctions of the operator S_z . The molecular wave function should be an eigenfunction of S^2 as well as S_z to satisfy the spectroscopic configuration for the state. Eigenvalues of S^2 determine the multiplicity of the molecular state, an important spectroscopic consideration.

To overcome this deficiency in the generalized solution for an open-shell state, the restricted treatment was introduced. This method, as the name implies, restricts the space functions of paired electrons to be identical. These restricted solutions are eigenfunctions of the commuting operators \mathcal{H} , S_z and S^2 . However, as a result of the restriction, they are not exact solutions of the generalized secular equations. Their validity, however, can be demonstrated if it can be shown that the generalized and restricted results for the same molecular state

agree within the limits of error of either method. For this reason, the results of generalized and restricted treatments for these states are compared in Table 6. Total energy results for the generalized function are uniformly less than or equal to those for the restricted function, as might be expected, but the difference is 0.009 a.u. at most and generally much less. Vertical transition energies calculated by the two methods are in fair agreement. Furthermore, these calculated results are within 1-2 ev. of the observed values in all cases except that of O_2^+ ($a^4 \pi_u$). For this state, our calculated result and that of Kotani⁽¹⁶⁾ deviate from the observed value by about 5 ev.

D. Conclusion

The restricted function for an open-shell state, though introducing an additional approximation in the solution of the appropriate secular equations, represents a pure spin state and results in total energies and transition energies in substantial agreement with those of the generalized function. These results for single configurations of open-shell states of N_2 and O_2 show that energies calculated in this way afford an agreement with experiment comparable to that for closed-shell states. In addition, this treatment provides a state function determined variationally for a given electronic configuration. The validity of these functions for open-shell states will be further demonstrated if they can successfully predict other electronic properties of these states.

In these calculations, we have tried to see how well we can represent each molecular state by a single AP function, in order to preserve the simple physical concepts of the MO theory. For this reason, we have restricted our consideration to states which can thus be described. The calculations can easily be extended, however, to include configuration interaction. Some of the excited states, for example, are best represented as a linear combination of AP functions. These results for a single function, however, agree sufficiently well with experiment.

FIGURE 1. CALCULATED ENERGY LEVELS FOR N_2

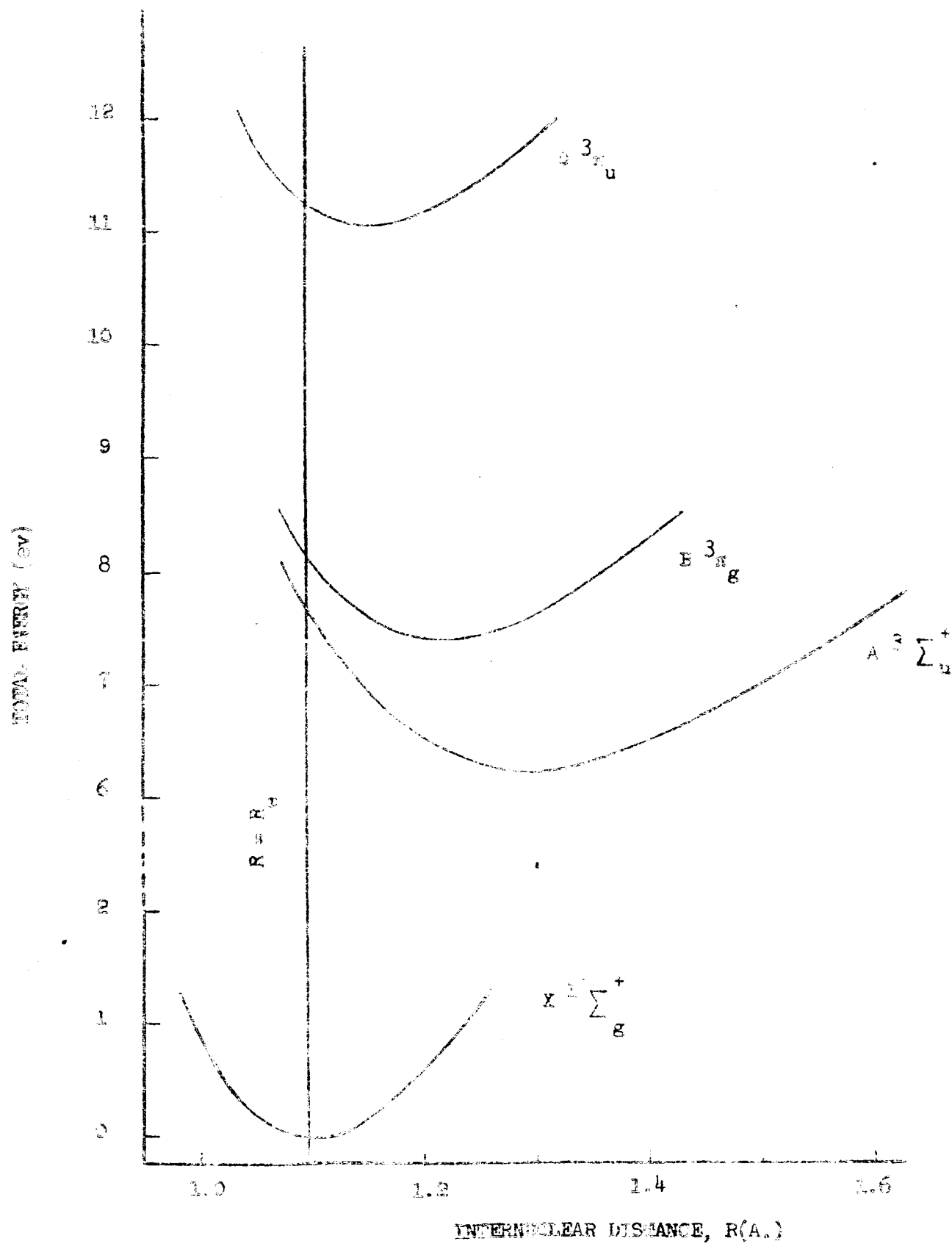


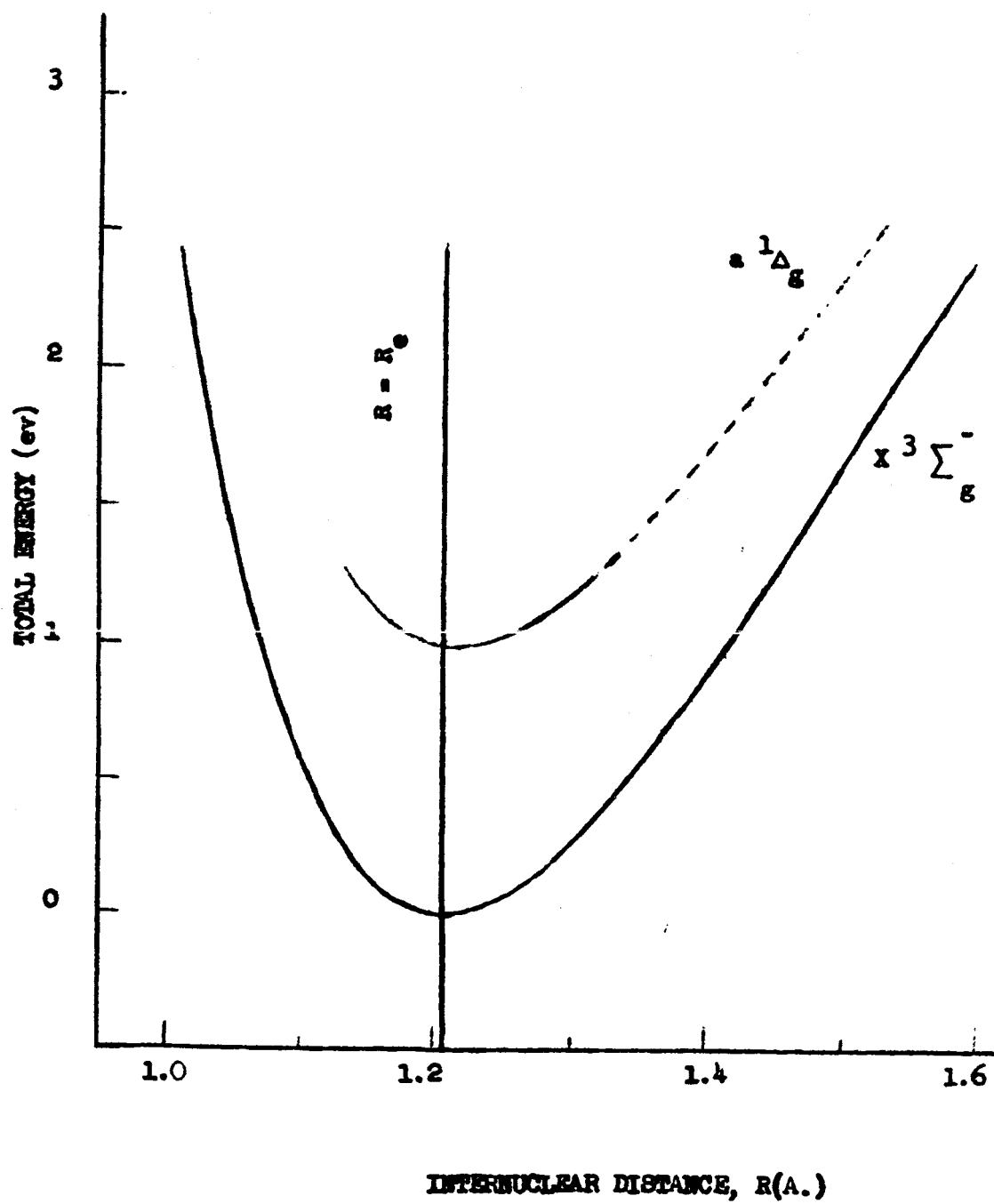
FIG. 2. POTENTIAL ENERGY CURVES FOR O_2 

TABLE 6

COMPARISON OF GENERALIZED AND RESTRICTED TREATMENTS

A. TOTAL ENERGY (a.u.)

<u>STATE</u>	<u>GENERALIZED</u>	<u>RESTRICTED</u>
$N_2, X \ ^1\Sigma_g^+$		-108.573572
$N_2, A \ ^3\Sigma_u^+$	-108.310805	-108.309100
$N_2, B \ ^3\Pi_g$	-108.302191	-108.298274
$N_2, C \ ^3\Pi_u$	-108.108547	-108.108545
$N_2^+, X \ ^2\Sigma_g^+$	-108.038262	-108.029387
$N_2^+, B \ ^2\Sigma_u^+$	-107.843224	-107.843229
$O_2, X \ ^3\Sigma_g^-$	-149.094159	-149.092076
$O_2, a \ ^1\Delta_g$		-149.010520
$O_2^+, X \ ^2\Pi_g$	-148.694655	-148.694117
$O_2^+, a \ ^4\Pi_u$	-148.671956	-148.668197

TABLE 6 (CON'T)

B. VERTICAL EXCITATION ENERGY (ev.)					
<u>STATE</u>	<u>GENERALIZED</u>		<u>RESTRICTED</u>		<u>OBSERVED</u>
	<u>$E^* - E^0$</u>	<u>$\epsilon_a^* - \epsilon_1^0$</u>	<u>$E^* - E^0$</u>	<u>$\epsilon_a^* - \epsilon_1^0$</u>	
$N_2, A \ ^3\Sigma_u^+$	7.15	7.18	7.19	7.25	7.70
$N_2, B \ ^3\Pi_g$	7.38	7.58	7.49	7.45	8.12
$N_2, C \ ^3\Pi_u$	12.65	12.66	12.65	12.66	11.25
$O_2, a \ ^1\Delta_g$			2.22	2.16	1.0

C. VERTICAL IONIZATION ENERGY (ev.)					
<u>STATE</u>	<u>GENERALIZED</u>		<u>RESTRICTED</u>		<u>OBSERVED</u>
	<u>$E^+ - E^0$</u>	<u>$-\epsilon_1^0$</u>	<u>$E^+ - E^0$</u>	<u>$-\epsilon_1^0$</u>	
$N_2^+, X \ ^2\Sigma_g^+$	14.56	14.81	14.80	14.81	15.58
$N_2^+, B \ ^2\Sigma_u^+$	19.87	19.87	19.88	19.87	18.67
$O_2^+, X \ ^2\Pi_g$	10.87	10.91	10.83	10.80	12.2
$O_2^+, a \ ^4\Pi_u$	11.49	11.56	11.53	11.50	16.1

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APPENDIX I
SELF-CONSISTENT FIELD MOLECULAR ORBITALS AND ENERGY VALUES
TABLE 7

$N_2 (X^1 \sum_g^+)$				$\epsilon_1^\alpha = \epsilon_1^\beta$
LCAO MO's				
$1\sigma_g$	0.9990 ($\sigma_g 1s$)	+0.0116 ($\sigma_g 2s$)	+0.0026 ($\sigma_g 2z$)	-15.7219
$2\sigma_g$	-0.0815 ($\sigma_g 1s$)	+0.6723 ($\sigma_g 2s$)	+0.3391 ($\sigma_g 2z$)	- 1.4527
$3\sigma_g$	-0.0430 ($\sigma_g 1s$)	-0.5589 ($\sigma_g 2s$)	+0.8531 ($\sigma_g 2z$)	- 0.5446
$1\sigma_u$	1.0025 ($\sigma_u 1s$)	+0.0272 ($\sigma_u 2s$)	+0.0121 ($\sigma_u 2z$)	-15.7197
$2\sigma_u$	-0.0106 ($\sigma_u 1s$)	-1.0207 ($\sigma_u 2s$)	+0.3759 ($\sigma_u 2z$)	- 0.7306
$1\pi_u$	0.8831 ($\pi_u x$)			- 0.5797
$1\bar{\pi}_u$	0.8831 ($\pi_u y$)			- 0.5797

TABLE 8

$N_2 (A^3 \sum_u^+)$				ϵ_1^α	ϵ_1^β
LCAO MO's					
$1\sigma_g$	0.9989 ($\sigma_g 1s$)	+0.0126 ($\sigma_g 2s$)	+0.0027 ($\sigma_g 2z$)	-15.6898	-15.6657
$2\sigma_g$	-0.0822 ($\sigma_g 1s$)	+0.6787 ($\sigma_g 2s$)	+0.3291 ($\sigma_g 2z$)	- 1.5122	- 1.3632
$3\sigma_g$	-0.0436 ($\sigma_g 1s$)	-0.5510 ($\sigma_g 2s$)	+0.8570 ($\sigma_g 2z$)	- 0.5547	- 0.4881
$1\sigma_u$	1.0028 ($\sigma_u 1s$)	+0.0303 ($\sigma_u 2s$)	+0.0135 ($\sigma_u 2z$)	-15.6884	-15.6641
$2\sigma_u$	-0.0173 ($\sigma_u 1s$)	-1.0771 ($\sigma_u 2s$)	+0.3167 ($\sigma_u 2z$)	- 0.7903	- 0.6543
$1\pi_u$	0.8831 ($\pi_u x$)			- 0.5935	- 0.5504
$1\bar{\pi}_u$	0.8831 ($\pi_u y$)			- 0.7642	
$1\bar{\pi}_g$	1.1803 ($\pi_g y$)			- 0.3131	

TABLE 9

<u>$N_2 (B^3\pi_g)$</u>		LCAO MO's			ϵ_1^α	ϵ_1^β
$1\sigma_g$	0.9990 ($\sigma_g 1s$)	+0.0127 ($\sigma_g 2s$)	+0.0020 ($\sigma_g 2z$)		-15.7014	-15.6728
$2\sigma_g$	-0.0806 ($\sigma_g 1s$)	+0.6937 ($\sigma_g 2s$)	+0.3053 ($\sigma_g 2z$)		- 1.4548	- 1.3499
$3\sigma_g$	-0.0452 ($\sigma_g 1s$)	-0.5320 ($\sigma_g 2s$)	+0.8658 ($\sigma_g 2z$)		- 0.6285	
$1\sigma_u$	1.0025 ($\sigma_u 1s$)	+0.0290 ($\sigma_u 2s$)	+0.0119 ($\sigma_u 2z$)		-15.7000	-15.6716
$2\sigma_u$	-0.0063 ($\sigma_u 1s$)	-1.0010 ($\sigma_u 2s$)	+0.3962 ($\sigma_u 2z$)		- 0.8337	- 0.5366
$1\pi_u$	0.8831 ($\pi_u x$)				- 0.7023	- 0.4882
$1\pi_g$	1.1803 ($\pi_g x$)				- 0.2707	
$1\pi_u$	0.8831 ($\pi_u y$)				- 0.5799	- 0.5340

TABLE 10

<u>$N_2 (C^3\pi_u)$</u>		LCAO MO's			ϵ_1^α	ϵ_1^β
$1\sigma_g$	0.9390 ($\sigma_g 1s$)	+0.0125 ($\sigma_g 2s$)	+0.0017 ($\sigma_g 2z$)		-15.6856	-15.6398
$2\sigma_g$	-0.0790 ($\sigma_g 1s$)	+0.7079 ($\sigma_g 2s$)	+0.2816 ($\sigma_g 2z$)		- 1.4187	- 1.3190
$3\sigma_g$	-0.0472 ($\sigma_g 1s$)	-0.5129 ($\sigma_g 2s$)	+0.8738 ($\sigma_g 2z$)		- 0.5991	- 0.3342
$1\sigma_u$	1.0024 ($\sigma_u 1s$)	+0.0282 ($\sigma_u 2s$)	+0.0112 ($\sigma_u 2z$)		-15.6841	-15.6374
$2\sigma_u$	-0.0072 ($\sigma_u 1s$)	-1.0066 ($\sigma_u 2s$)	+0.3905 ($\sigma_u 2z$)		- 0.8242	
$1\pi_u$	0.8831 ($\pi_u x$)				- 0.6918	- 0.4540
$1\pi_g$	1.1803 ($\pi_g x$)				- 0.2654	
$1\pi_u$	0.8831 ($\pi_u y$)				- 0.5693	

TABLE 11

$N_2^+ (X^2 \sum_g^+)$		LCAO MO's			ϵ_1^α	ϵ_1^β
$1\sigma_g$	0.9990 ($\sigma_g 1s$)	+0.0113 ($\sigma_g 2s$)	+0.0022 ($\sigma_g 2z$)		-16.4099	-16.3948
$2\sigma_g$	-0.0817 ($\sigma_g 1s$)	+0.6613 ($\sigma_g 2s$)	+0.3556 ($\sigma_g 2z$)		- 1.9952	- 1.9475
$3\sigma_g$	-0.0412 ($\sigma_g 1s$)	-0.5718 ($\sigma_g 2s$)	+0.8464 ($\sigma_g 2z$)		- 1.1314	
$1\sigma_u$	1.0023 ($\sigma_u 1s$)	+0.0257 ($\sigma_u 2s$)	+0.0109 ($\sigma_u 2z$)		-16.4077	-16.3935
$2\sigma_u$	-0.0061 ($\sigma_u 1s$)	-0.9872 ($\sigma_u 2s$)	+0.4103 ($\sigma_u 2z$)		- 1.2895	- 1.0658
$1\pi_u$	0.8831 ($\pi_u x$)				- 1.0983	- 1.0700
$1\bar{\pi}_u$	0.8831 ($\pi_u y$)				- 1.0983	- 1.0700

TABLE 12

$N_2^+ (B^2 \sum_u^+)$		LCAO MO's			ϵ_1^α	ϵ_1^β
$1\sigma_g$	0.9991 ($\sigma_g 1s$)	+0.0111 ($\sigma_g 2s$)	+0.0020 ($\sigma_g 2z$)		-16.4002	-16.3694
$2\sigma_g$	-0.0806 ($\sigma_g 1s$)	+0.6721 ($\sigma_g 2s$)	+0.3394 ($\sigma_g 2z$)		- 1.9681	- 1.9213
$3\sigma_g$	-0.0427 ($\sigma_g 1s$)	-0.5591 ($\sigma_g 2s$)	+0.8530 ($\sigma_g 2z$)		- 1.1064	- 0.8704
$1\sigma_u$	1.0022 ($\sigma_u 1s$)	+0.0251 ($\sigma_u 2s$)	+0.0105 ($\sigma_u 2z$)		-16.3980	-16.3670
$2\sigma_u$	-0.0076 ($\sigma_u 1s$)	-0.9970 ($\sigma_u 2s$)	+0.4003 ($\sigma_u 2z$)		- 1.2801	
$1\pi_u$	0.8831 ($\pi_u x$)				- 1.0927	- 1.0424
$1\bar{\pi}_u$	0.8831 ($\pi_u y$)				- 1.0927	- 1.0424

TABLE 13

$\underline{O_2 (\pi^3 \Sigma_g^-)}$		ICAO MO's			ϵ_1^α	ϵ_1^β
$1\sigma_g$	0.9996 ($\sigma_g 1s$)	+0.0127 ($\sigma_g 2s$)	+0.0002 ($\sigma_g 2z$)		-20.6305	-20.5997
$2\sigma_g$	-0.0410 ($\sigma_g 1s$)	+0.8054 ($\sigma_g 2s$)	+0.2153 ($\sigma_g 2z$)		- 1.5986	- 1.4750
$3\sigma_g$	0.0206 ($\sigma_g 1s$)	+0.4232 ($\sigma_g 2s$)	-0.8749 ($\sigma_g 2z$)		- 0.5965	- 0.5259
$1\sigma_u$	1.0006 ($\sigma_u 1s$)	+0.0204 ($\sigma_u 2s$)	+0.0065 ($\sigma_u 2z$)		-20.6311	-20.5994
$2\sigma_u$	0.0033 ($\sigma_u 1s$)	+1.0798 ($\sigma_u 2s$)	-0.2010 ($\sigma_u 2z$)		- 1.0820	- 0.8862
$1\pi_u$	0.9340 ($\pi_u x$)				- 0.6965	- 0.4227
$1\pi_g$	1.0824 ($\pi_g x$)				- 0.3969	
$1\bar{\pi}_u$	0.9340 ($\pi_u y$)				- 0.6965	- 0.4227
$1\bar{\pi}_g$	1.0824 ($\pi_g y$)				- 0.3969	

TABLE 14

$\underline{O_2 (s^1 \Delta_g)}$		ICAO MO's			$\epsilon_1^\alpha = \epsilon_1^\beta$
$1\sigma_g$	0.9996 ($\sigma_g 1s$)	+0.0119 ($\sigma_g 2s$)	+0.0004 ($\sigma_g 2z$)		-20.6212
$2\sigma_g$	-0.0408 ($\sigma_g 1s$)	+0.7929 ($\sigma_g 2s$)	+0.2403 ($\sigma_g 2z$)		- 1.5412
$3\sigma_g$	0.0198 ($\sigma_g 1s$)	+0.4462 ($\sigma_g 2s$)	-0.8683 ($\sigma_g 2z$)		- 0.5671
$1\sigma_u$	1.0006 ($\sigma_u 1s$)	+0.0189 ($\sigma_u 2s$)	+0.0063 ($\sigma_u 2z$)		-20.6213
$2\sigma_u$	0.0030 ($\sigma_u 1s$)	+1.0630 ($\sigma_u 2s$)	-0.2302 ($\sigma_u 2z$)		- 0.9835
$1\pi_u$	0.9340 ($\pi_u x$)				- 0.6266
$1\pi_g$	1.0824 ($\pi_g x$)				- 0.3174
$1\bar{\pi}_u$	0.9340 ($\pi_u y$)				- 0.5000

TABLE 15

$O_2^+ (X^2 \pi_g)$				ϵ_1^α	ϵ_1^β
LCAO MO's					
$1\sigma_g$	0.9996 ($\sigma_g 1s$)	+0.0115 ($\sigma_g 2s$)	+0.0005 ($\sigma_g 2z$)	-21.4036	-21.3882
$2\sigma_g$	-0.0409 ($\sigma_g 1s$)	+0.7818 ($\sigma_g 2s$)	+0.2614 ($\sigma_g 2z$)	- 2.1692	- 2.1095
$3\sigma_g$	0.0190 ($\sigma_g 1s$)	+0.4654 ($\sigma_g 2s$)	-0.8622 ($\sigma_g 2z$)	- 1.1534	- 1.1160
$1\sigma_u$	1.0006 ($\sigma_u 1s$)	+0.0184 ($\sigma_u 2s$)	+0.0062 ($\sigma_u 2z$)	-21.4037	-21.3879
$2\sigma_u$	0.0055 ($\sigma_u 1s$)	+1.0876 ($\sigma_u 2s$)	-0.1873 ($\sigma_u 2z$)	- 1.5838	- 1.4847
$1\pi_u$	0.9340 ($\pi_u x$)			- 1.2654	- 1.0146
$1\pi_g$	1.0824 ($\pi_g x$)			- 0.9735	
$1\bar{\pi}_u$	0.9340 ($\pi_u y$)			- 1.0882	- 1.0652

TABLE 16

$O_2^+ (a^4 \pi_u)$				ϵ_1^α	ϵ_1^β
LCAO MO's					
$1\sigma_g$	0.9996 ($\sigma_g 1s$)	+0.0124 ($\sigma_g 2s$)	+0.0004 ($\sigma_g 2z$)	-21.3753	-21.3322
$2\sigma_g$	-0.0416 ($\sigma_g 1s$)	+0.7879 ($\sigma_g 2s$)	+0.2500 ($\sigma_g 2z$)	- 2.2317	- 2.0116
$3\sigma_g$	0.0192 ($\sigma_g 1s$)	+0.4550 ($\sigma_g 2s$)	-0.8656 ($\sigma_g 2z$)	- 1.1671	- 1.0593
$1\sigma_u$	1.0006 ($\sigma_u 1s$)	+0.0201 ($\sigma_u 2s$)	+0.0067 ($\sigma_u 2z$)	-21.3759	-21.3321
$2\sigma_u$	0.0061 ($\sigma_u 1s$)	+1.1096 ($\sigma_u 2s$)	-0.1470 ($\sigma_u 2z$)	- 1.6665	- 1.3936
$1\pi_u$	0.9340 ($\pi_u x$)			- 1.2774	- 0.9787
$1\pi_g$	1.0824 ($\pi_g x$)			- 0.9857	
$1\bar{\pi}_u$	0.9340 ($\pi_u y$)			- 1.3272	
$1\bar{\pi}_g$	1.0824 ($\pi_g y$)			- 1.0364	

APPENDIX II

The total electronic energy of the molecule is given by the expression

$$E_{el} = \sum_i^{\alpha+\beta} H_i + 1/2 \sum_i^{\alpha+\beta} \sum_j^{\alpha+\beta} J_{ij} - 1/2 \left(\sum_{i,j}^{\alpha} + \sum_{i,j}^{\beta} \right) K_{ij} \quad (15)$$

Since each self consistent ϵ_i represents

$$\epsilon_i^{\alpha(\beta)} = H_i^{\alpha(\beta)} + \sum_j^{\alpha+\beta} J_{ij} - \sum_j^{\alpha(\beta)} K_{ij}, \quad (16)$$

we can see that (15) becomes

$$E_{el} = 1/2 \sum_i^{\alpha} (\epsilon_i^{\alpha} + H_i^{\alpha}) + 1/2 \sum_i^{\beta} (\epsilon_i^{\beta} + H_i^{\beta}) \quad (17)$$

where

$$H_i^{\alpha} = \underline{a}_i^{\alpha*} H \underline{a}_i^{\alpha}; \quad H_i^{\beta} = \underline{a}_i^{\beta*} H \underline{a}_i^{\beta} \quad (18)$$

For a closed-shell state, (17) reduces to

$$E_{el} = \sum_i^{\alpha} (\epsilon_i^{\alpha} + H_i^{\alpha}) = \sum_i^{\beta} (\epsilon_i^{\beta} + H_i^{\beta}) \quad (19)$$

The total potential energy of the molecule is obtained by adding the nuclear repulsion term, $Z_a Z_b / r_{ab}$, to expressions (17) and (19), where "a" and "b" index nuclei and Z is the nuclear charge.